



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP98/05104  <b>(22) International Filing Date:</b> 5 August 1998 (05.08.98)  <b>(30) Priority Data:</b> 9704573-0                      29 August 1997 (29.08.97)                      BR  <b>(71) Applicant (for AU BB CA CY GB GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only):</b> UNILEVER PLC [GB/GB]; Unilever, Blackfriars, London EC4P 4BQ (GB).  <b>(71) Applicant (for all designated States except AU BB CA CY GB GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).  <b>(72) Inventors:</b> VELAZQUEZ GOLINO, Maria del Carmen; Apartamento 12, Rua Dr Francisco Jose Longo, 281, Saude, CEP-São Paulo, SP (BR). POLEZEL, Marcio, Antonio; Rua Antonio Amstalden, 483, Vila Suica, CEP-Indaiatuba, SP (BR).  <b>(74) Agent:</b> GRIFFITHS, Helen, Sarah; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KB, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> HAIR TREATMENT COMPOSITIONS  <b>(57) Abstract</b>  The invention provides a hair treatment composition suitable for application to dark hair, which composition comprises at least one melanin or melanin-type compound, characterised in that the melanin or melanin-type compound is of botanical origin. Preferably, the melanin source is a hydroglycolic extract of plants selected from at least three, most preferably all four, of the following species: <i>Viola</i> (violet), <i>Vaccinium myrtillus</i> (bilberry), <i>Indigofera tinctoria</i> (indigo) and <i>Sarothamnus scoparius</i> . The composition is used to impart a "blue" shine to dark hair and protect hair against the damaging effects of UV radiation.		

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HAIR TREATMENT COMPOSITIONSFIELD OF THE INVENTION

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The present invention relates to hair treatment compositions. In particular the invention relates to hair treatment compositions including melanin of botanical origin. The compositions are particularly suitable for application to hair which is naturally dark brown to black.

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BACKGROUND AND PRIOR ART

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Exposure to sunlight and harsh chemical treatments can give dark hair a reddish or "burnt" look, whereas a "bluish" shine to the hair is frequently desired by dark haired consumers.

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Various patent publications disclose the use of melanin products as temporary hair colourants. WO94/25531 describes finely divided melanin pigments for colouring hair produced by solubilising and precipitating natural melanin extracted from keratin fibres or cuttle-fish ink. JP 6128129 describes a hair colouring agent containing natural melanin which protects hair from damage caused by UV rays.

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A problem with melanin pigment extracted from animal sources is that firstly it is very costly and secondly it is composed basically of black and brown pigments which do not reflect visible light and do not provide the desirable "blue" shine to the hair as mentioned above.

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Alternatively synthetic melanin may be produced by oxidative polymerisation of an amino or hydroxy-indole derivative. JP 3077813 describes a hair composition containing melanin pigment obtained by enzymatic action of bacterial tyrosinase or laccase on phenols. Such synthetic pigments have not  
5 found widespread use in consumer products since they are prohibitively expensive.

The present inventors have found that botanically-derived  
10 melanins or melanin-type compounds can provide hair with improved colour maintenance, blue shine and protection against light and UV-radiation. Furthermore, such extracts are available at low cost and are particularly suitable for formulation into hair treatment compositions, especially  
15 those for application to hair which is naturally dark brown to black.

#### SUMMARY OF THE INVENTION

20 The present invention provides a hair treatment composition suitable for application to dark hair, which composition comprises at least one melanin or melanin-type compound, characterised in that the melanin or melanin-type compound is of botanical origin.

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#### DETAILED DESCRIPTION OF THE INVENTION

##### (i) Melanin or Melanin-Type Compounds of Botanical Origin

30 A preferred source of melanin or melanin-type compounds of botanical origin is a blend comprising three types of botanical extract, said types being extracts of plants

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belonging to the *Papilionoidea*, *Violacea*, and *Ericaceas* families respectively.

Of the *Papilionoidea* family, preferred species include

- 5 *Indigofera tinctoria* and *Sarathamnus scoparus*. These may be further characterised as follows:

*Indigofera tinctoria* is a leguminous plant which produces a melanin called indigotine. This is the "indigo blue" used  
10 for centuries as a natural dye. Chemically, this substance resembles human melanin in that it is also one of the general class of compounds termed benzophenones. Functionally, it performs a similar colouring and protective  
15 role.

*Sarathamnus scoparus* is also a leguminous plant. It is rich in dark melanin, which is responsible for the black colour of the ripe legumes.

- 20 Of the *Violacea* family, preferred species include the violets: *Viola sp.* This is a flowering herb whose intensely violet coloured flowers are rich in anthocyanidines and anthocyanines. These are also of the benzophenone class and serve as precursors for melanin pigments with colouring and  
25 protective functions.

Of the *Ericaceas* family, preferred species include *Vaccinium myrtillus* (bilberry). This is a woody plant bearing bluish black fruit. Chemically the colouring of the fruit derives  
30 from the melanin precursor pigments, anthocyanidines and anthocyanines, and a flavonoid designated as myrtiline, a violet pigment with a strong anti-free radical activity. The

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flavonoids may also be described chemically as benzophenones, and therefore of the same chemical class as human dark melanin.

- 5 Most preferred is a hydroglycolic extract of plants selected from at least three, most preferably all four, of the following species: *Viola*(violet), *Vaccinium myrtillus* (bilberry), *Indigofera tinctoria*(indigo) and *Sarathamnus scoparus*. The inventors have found that this type of extract  
10 is particularly effective due to synergism between the individual components and also the improved stability of the extract towards oxidation. For example, *Indigofera tinctoria* extract on its own gives a blue colour tone to the hair due to the presence of a melanin called indigotine. However,  
15 this pigment is susceptible to rapid oxidation on exposure to light, leading to a reduction in the hair's blue shine. However, when associated with the other plant extracts as described above, a photostabilisation of the blue colour is observed. Consequently a blue reflection occurs with higher  
20 durability.

The preferred three or four-component hydroglycolic extract as described above is therefore particularly suitable for incorporation into a hair treatment composition to provide enhanced hair colour maintenance, durable blue shine reflection and protection against the damaging effects of UV radiation. A suitable level of incorporation ranges from 0.03 to 5%, preferably 0.005 to 2%, ideally 0.01 to 1%, by weight based on the total weight of the hair treatment composition.

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(ii) Product Form

Hair treatment compositions according to the invention may suitably take the form of shampoos, conditioners, sprays, mousses or lotions. Preferred hair treatment composition forms are shampoos and conditioners.

Shampoo Compositions

A particularly preferred hair treatment composition in accordance with the invention is a shampoo composition.

- Cleansing Surfactant

Such a shampoo composition will comprise one or more cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair. Further surfactants may be present as an additional ingredient if sufficient for cleansing purposes is not provided as emulsifying agent for oily or hydrophobic components (such as silicones) which may typically be present in the shampoo.

It is preferred that shampoo compositions of the invention comprise at least one further surfactant (in addition to that used as emulsifying agent) to provide a cleansing benefit.

Suitable cleansing surfactants, which may be used singularly or in combination, are selected from anionic, amphoteric and zwitterionic surfactants, and mixtures thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

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Examples of anionic surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule.

Typical anionic surfactants for use in shampoos of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1 EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

Examples of amphoteric and zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.



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The shampoo composition can also include co-surfactants, to help impart aesthetic, physical or cleansing properties to the composition. A preferred example is a nonionic surfactant, which can be included in an amount ranging from 0% to about 5% by weight based on total weight.

For example, representative nonionic surfactants that can be included in shampoo compositions of the invention include condensation products of aliphatic ( $C_8 - C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Other representative nonionics include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in shampoo compositions of the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:



wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about  $C_5$  to about  $C_{20}$ . Preferably R represents a mean alkyl chain

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length of from about C<sub>8</sub> to about C<sub>12</sub>. Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from C<sub>5</sub> or C<sub>6</sub> monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

The degree of polymerisation, n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies in the range of from about 1.1 to about 2. Most preferably the value of n lies in the range of from about 1.3 to about 1.5.

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

The total amount of surfactant (including any co-surfactant, and/or any emulsifying agent) in shampoo compositions of the invention is generally from 0.1 to 50% by weight, preferably from 5 to 30%, more preferably from 10% to 25% by weight of the total shampoo composition.

- Cationic Polymer

A cationic polymer is a preferred ingredient in shampoo compositions of the invention, for enhancing conditioning performance of the shampoo. Typically such a polymer enhances deposition of conditioning components such as silicone from the shampoo composition onto the intended site during use, i.e. the hair and/or the scalp.

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The cationic polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between 5 000 and 10 000 000, typically at least 10 000 and preferably in the range 100 000 to about 2 000 000. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give a polymer having a cationic charge density in the required range.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

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Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic polymers include, for example:

- copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g. chloride salt), referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, (CTFA) as Polyquaternium-16. This material is commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g. LUVIQUAT FC 370);
- copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate, referred to in the industry (CTFA) as Polyquaternium-11. This material is available commercially from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N);
- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively;
- mineral acid salts of amino-alkyl esters of homo-and copolymers of unsaturated carboxylic acids having from 3

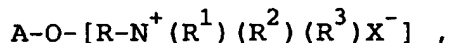
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to 5 carbon atoms, (as described in U.S. Patent 4,009,256);

- cationic polyacrylamides (as described in W095/22311).

Other cationic polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives.

Cationic polysaccharide polymers suitable for use in compositions of the invention include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof.  $R^1$ ,  $R^2$  and  $R^3$  independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in  $R^1$ ,  $R^2$  and  $R^3$ ) is preferably about 20 or less, and X is an anionic counterion.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trade mark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10.

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Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimonium chloride (Commercially available from Rhone-Poulenc in their JAGUAR trademark series).

Examples are JAGUAR C13S, which has a low degree of substitution of the cationic groups and high viscosity. JAGUAR C15, having a moderate degree of substitution and a low viscosity, JAGUAR C17 (high degree of substitution, high viscosity), JAGUAR C16, which is a hydroxypropylated cationic guar derivative containing a low level of substituent groups as well as cationic quaternary ammonium groups, and JAGUAR 162 which is a high transparency, medium viscosity guar having a low degree of substitution.

Preferably the cationic polymer is selected from cationic cellulose and cationic guar derivatives. Particularly preferred cationic polymers are JAGUAR C13S, JAGUAR C15, JAGUAR C17 and JAGUAR C16 and JAGUAR C162.

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Conditioners

Compositions in accordance with the invention may also be formulated as conditioners for the treatment of hair (typically after shampooing) and subsequent rinsing.

- Conditioning Surfactant

Such a conditioner will comprise one or more conditioning surfactants which are cosmetically acceptable and suitable for topical application to the hair.

Suitable conditioning surfactants are selected from cationic surfactants, used singly or in admixture. Examples include quaternary ammonium hydroxides or salts thereof, e.g. chlorides.

Suitable cationic surfactants for use in hair conditioners of the invention include cetyltrimethylammonium chloride, behenyltrimethylammonium chloride, cetylpyridinium chloride, tetramethylammonium chloride, tetraethylammonium chloride, octyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium chloride, octyldimethylbenzylammonium chloride, decyldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, didodecyldimethylammonium chloride, dioctadecyldimethylammonium chloride, tallowtrimethylammonium chloride, cocotrimethylammonium chloride, and the corresponding hydroxides thereof. Further suitable cationic surfactants include those materials having the CTFA designations Quaternium-5, Quaternium-31 and Quaternium-18. Mixtures of any of the foregoing materials may also be

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suitable. A particularly useful cationic surfactant for use in hair conditioners of the invention is cetyltrimethylammonium chloride, available commercially, for example as DEHYQUART, ex Henkel.

In conditioners of the invention, the level of cationic surfactant is preferably from 0.01 to 10%, more preferably 0.05 to 5%, most preferably 0.1 to 2% by weight of the composition.



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- Fatty Alcohol

Conditioners of the invention advantageously incorporate a fatty alcohol material. The combined use of fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, in which the cationic surfactant is dispersed.

Representative fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 20. Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol and mixtures thereof. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

The level of fatty alcohol material in conditioners of the invention is conveniently from 0.01 to 10%, preferably from 0.1 to 5% by weight of the composition. The weight ratio of cationic surfactant to fatty alcohol is suitably from 10:1 to 1:10, preferably from 4:1 to 1:8, optimally from 1:1 to 1:4.

Silicone

Silicone is a particularly preferred ingredient in hair treatment compositions of the invention. In particular, hair shampoos and conditioners of the invention will preferably also comprise emulsified particles of silicone, for enhancing conditioning performance. The silicone is insoluble in the aqueous matrix of the composition and so is present in an emulsified form, with the silicone present as dispersed particles.

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Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention (particularly shampoos and conditioners) are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188. These materials can impart body, volume and stylability to hair, as well as good wet and dry conditioning.

The viscosity of the emulsified silicone itself (not the emulsion or the final hair conditioning composition) is typically at least 10,000 cst. In general we have found that conditioning performance increases with increased viscosity. Accordingly, the viscosity of the silicone itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed  $10^9$  cst for ease of formulation.

Emulsified silicones for use in hair shampoos and conditioners of the invention will typically have an average silicone particle size in the composition of less than 30, preferably less than 20, more preferably less than 10 microns. We have found that reducing the particle size generally improves conditioning performance. Most preferably the average silicone particle size of the emulsified silicone in the composition is less than 2 microns, ideally it ranges from 0.01 to 1 micron. Silicone

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emulsions having an average silicone particle size of  $\leq 0.15$  microns are generally termed microemulsions.

Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments.

Suitable silicone emulsions for use in the invention are also commercially available in a pre-emulsified form.

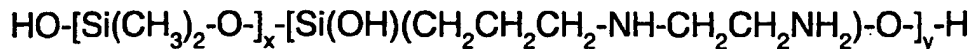
Examples of suitable pre-formed emulsions include emulsions DC2-1766, DC2-1784, and microemulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/microemulsions of dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. A preferred example is the material available from Dow Corning as DC X2-1787, which is an emulsion of cross-linked dimethiconol gum. A further preferred example is the material available from Dow Corning as DC X2-1391, which is a microemulsion of cross-linked dimethiconol gum.

A further preferred class of silicones for inclusion in shampoos and conditioners of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing at least one primary, secondary or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include:

- (i) polysiloxanes having the CTFA designation "amodimethicone", and the general formula:

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in which x and y are numbers depending on the molecular weight of the polymer, generally such that the molecular weight is between about 5,000 and 500,000.

(ii) polysiloxanes having the general formula:



in which:

G is selected from H, phenyl, OH or C<sub>1-8</sub> alkyl, e.g. methyl;

a is 0 or an integer from 1 to 3, preferably 0;

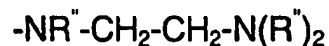
b is 0 or 1, preferably 1;

m and n are numbers such that (m + n) can range from 1 to 2000, preferably from 50 to 150;

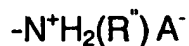
m is a number from 1 to 2000, preferably from 1 to 10;

n is a number from 0 to 1999, preferably from 49 to 149, and

R' is a monovalent radical of formula -C<sub>q</sub>H<sub>2q</sub>L in which q is a number from 2 to 8 and L is an aminofunctional group selected from the following:



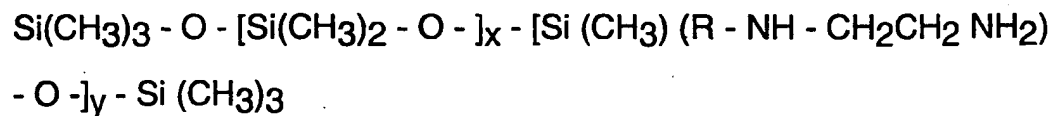
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in which  $R''$  is selected from H, phenyl, benzyl, or a saturated monovalent hydrocarbon radical, e.g.  $C_{1-20}$  alkyl, and

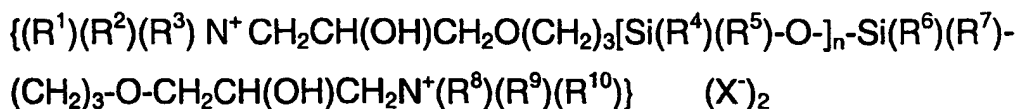
A is a halide ion, e.g. chloride or bromide.

Suitable amino functional silicones corresponding to the above formula include those polysiloxanes termed "trimethylsilylamodimethicone" as depicted below, and which are sufficiently water insoluble so as to be useful in compositions of the invention:



wherein  $x + y$  is a number from about 50 to about 500, and wherein R is an alkylene group having from 2 to 5 carbon atoms. Preferably, the number  $x + y$  is in the range of from about 100 to about 300.

(iii) quaternary silicone polymers having the general formula:



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wherein  $R^1$  and  $R^{10}$  may be the same or different and may be independently selected from H, saturated or unsaturated long or short chain alk(en)yl, branched chain alk(en)yl and  $C_5-C_8$  cyclic ring systems;

$R^2$  thru'  $R^9$  may be the same or different and may be independently selected from H, straight or branched chain lower alk(en)yl, and  $C_5-C_8$  cyclic ring systems;

n is a number within the range of about 60 to about 120, preferably about 80, and

$X^-$  is preferably acetate, but may instead be for example halide, organic carboxylate, organic sulphonate or the like. Suitable quaternary silicone polymers of this class are described in EP-A-0 530 974.

Amino functional silicones suitable for use in shampoos and conditioners of the invention will typically have a mole % amine functionality in the range of from about 0.1 to about 8.0 mole %, preferably from about 0.1 to about 5.0 mole %, most preferably from about 0.1 to about 2.0 mole %. In general the amine concentration should not exceed about 8.0 mole % since we have found that too high an amine concentration can be detrimental to total silicone deposition and therefore conditioning performance.

The viscosity of the amino functional silicone is not particularly critical and can suitably range from about 100 to about 500,000 cst.

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Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166, DC2-8466, and DC2-8950-114 (all ex Dow Corning), and GE 1149-75, (ex General Electric Silicones).

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.

Suitably such pre-formed emulsions will have an average amino functional silicone particle size in the shampoo composition of less than 30, preferably less than 20, more preferably less than 10 microns. Again, we have found that reducing the particle size generally improves conditioning performance. Most preferably the average amino functional silicone particle size in the composition is less than 2 microns, ideally it ranges from 0.01 to 1 micron. Silicone emulsions having an average silicone particle size of  $\leq 0.15$  microns are generally termed microemulsions.

Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC929 Cationic Emulsion, DC939 Cationic Emulsion, and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

An example of a quaternary silicone polymer useful in the present invention is the material K3474, ex Goldschmidt.

For shampoo compositions according to the invention intended for the treatment of "mixed" hair (i.e. greasy roots and dry

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ends), it is particularly preferred to use a combination of amino functional and non-amino functional silicone in compositions of the invention, especially when these are in the form of shampoo compositions. In such a case, the weight ratio of amino functional silicone to non-amino functional silicone will typically range from 1:2 to 1:20, preferably 1:3 to 1:20, more preferably 1:3 to 1:8. The total amount of silicone incorporated into compositions of the invention depends on the level of conditioning desired and the material used. A preferred amount is from 0.01 to about 10% by weight of the total composition although these limits are not absolute. The lower limit is determined by the minimum level to achieve conditioning and the upper limit by the maximum level to avoid making the hair and/or skin unacceptably greasy.

We have found that a total amount of silicone of from 0.3 to 5%, preferably 0.5 to 3%, by weight of the total composition is a suitable level.

#### (iii) Optional Ingredients

Compositions of this invention may contain any other ingredient normally used in hair treatment formulations. These other ingredients may include viscosity modifiers, preservatives, colouring agents, polyols such as glycerine and polypropylene glycol, chelating agents such as EDTA, antioxidants such as vitamin E acetate, fragrances, antimicrobials and sunscreens. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to about 5% by weight of the total composition.



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Preferably, compositions of this invention also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2%, preferably up to 1%, by weight of the total composition.

Among suitable hair care adjuvants, are:

- (i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g. fruit extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.
- (ii) hair fibre benefit agents. Examples are:

- ceramides, for moisturising the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A preferred ceramide is Ceramide II, ex Quest. Mixtures of ceramides may also be suitable, such as Ceramides LS, ex Laboratoires Serobiologiques.

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- fatty acids, for cuticle repair and damage prevention. Examples are branched chain fatty acids such as 18-methyleicosanoic acid and other homologues of this series, straight chain fatty acids such as stearic, myristic and palmitic acids, and unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid and arachidonic acid. A preferred fatty acid is oleic acid. The fatty acids may be added singly, as mixtures, or in the form of blends derived from extracts of, e.g. lanolin.

Mixtures of any of the above active ingredients may also be used.

The invention is further illustrated by way of the following non-limitative examples, in which all percentages quoted are by weight based on total weight unless otherwise stated:

EXAMPLESExample 1Preparation of an extract of melanin of botanical origin

Complete extraction of the pigments of the plants *Viola*(violet), *Vaccinium myrtillus* (bilberry), *Indigofera tinctoria*(indigo) and *Sarathamnus scoparus* was performed by hydroglycolic percolation in the ratio of 1:2. The  
5 individual plants were used in roughly equal proportions.

The extract so obtained had the following physical-chemical characteristics.

10	Appearance (25°C)	Non-viscous liquid
	Colour	Dark blue
	Odour	Floral
	pH(at 25°C)	5.00 - 6.00
	Solids content (%w/w) *	0.50 - 3.00
15	Density ( g/cm <sup>3</sup> )	0.950 - 1.150

\* Determined after heating 10g sample of extract to 180°C for 12 hours

20 The composition of the above hydroglycolic extract exhibits a synergistic effect between the individual components, as regards certain beneficial properties as demonstrated in the following Examples:

25 Example 2

## Protection against UV radiation

Individually taken, the components of the extract of Example 1 absorb UV radiation in the ranges given below:

5

<i>Indigofera tinctoria</i>	258 nm to 408 nm range
extract	with maximum absorbency at
	304 nm

10 *Sarathamnus scoparus* 250 nm to 300 nm range with  
extract maximum absorbency at 256 nm

Viola sp extract                      258 nm to 400 nm range with  
maximum absorbency at 276 nm

15

*Vaccinium myrtillus* 264 nm to 368 nm with maximum  
extract absorbency at 282 nm

20 The extract of Example 1, being a blend of the above four  
extracts, has an absorption range between 266 nm and 416 nm,  
i.e. a broader UV absorption range than the individual  
extracts. The maximum absorbency of the extract of Example 1  
occurs at 286 nm. A curve of intensity of absorbance versus  
25 wavelength when plotted for the extract of Example 1 shows a  
much higher intensity of absorbance at this wavelength  
compared to the intensity maxima observed with equivalent  
curves plotted for each of the individual extracts.

30 Spectral analysis shows that the extract of Example 1  
exhibits a synergistic effect between the chromophorous

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components of the individual extracts which are combined in the extract of Example 1.

5 This synergistic effect observed for the extract of Example 1 is particularly advantageous in the context of hair treatment compositions, since it provides for a higher protection against UV radiation, because of the increased intensity and range of radiation absorption. UV rays, mainly UVB rays in the wavelength range of 290 nm to 320 nm and UVA  
10 rays in the wavelength range of 320 nm to 400 nm are extremely damaging to the hair, and can lead to its breakage and discoloration.

### Example 3

15

#### Determination of the protective effect of the extract of Example 1 towards UV induced lipid oxidation

20 The following test uses methodology originally described by Hammerschmidt & Prati (1979) for determining the level of preservation of linoleic acid by anti-oxidant agents.

The following solutions were prepared:

- 25 i) Blank (control): 20 mg linoleic acid, 200 mg Polysorbate 20, in 50 ml distilled water.
- ii) Standard : 100 ppm (0.01wt%) alpha-tocopherol, 50 ppm (0.005wt%) ascorbic acid, 20 mg linoleic acid, 200 mg  
30 Polysorbate 20, in 50 ml distilled water.

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iii) Test: = 100 to 3000 ppm (0.01 - 3wt%) extract of  
Example 1, 20 mg of linoleic acid ,200 mg Polysorbate 20 in  
50 ml distilled water.

- 5 All solutions were homogenised for 30 seconds and tested for the effects of exposure to ultraviolet radiation at 254 nm. Samples were incubated for 30 minute periods, doing separate runs with and without UV radiation for each solution.
- 10 After incubation, the optical density (absorbency) of the samples at 232 nm (wavelength of maximum absorbency of conjugated dienes) was measured in a 1 cm cuvette in a spectrophotometer (UV-Vis Lambda 3, ex Perkin Elmer).

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Results:

Table 1 - Effect of extract of Example 1 ("Extract") at various concentrations, after 30 min incubation.

5

("Difference" denotes the value obtained by subtracting the "without UV" measurement from the "with UV" measurement for a particular sample)

10	<u>Concentration(wt%)</u>	<u>Without UV</u>	<u>With UV</u>	<u>Difference</u>
	Extract 0.01	0.149	0.320	0.171
	Extract 0.02	0.017	0.059	0.042
	Extract 0.03	0.056	0.097	0.041
15	Extract 0.1	0.212	0.166	-0.046
	Extract 0.2	0.555	0.528	-0.027
	Extract 0.3	0.893	0.871	-0.022
	Control	0.488	1.393	0.905
20	Standard	2.607	2.615	0.008

The results show that at concentrations higher than 0.03wt% (300ppm), the extract of Example 1 shows an excellent anti-oxidant effect which compares favourably with standard and  
25 widely used anti-oxidants such as alpha-tocopherol.

This anti-oxidant effect observed for the extract of Example 1 is especially advantageous in the context of hair treatment compositions, since it provides for protection of  
30 natural hair lipids against oxidation and damage.

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Example 4

A shampoo composition was prepared by mixing the following components in the amounts stated.

<u>Component</u>	<u>% by weight</u>
Sodium lauryl ether sulphate 2EO	14.0
Cocamidopropyl betaine	2.0
Jaguar C13S	0.2
CARBOPOL ETD 2020	0.4
Extract of Example 1	0.25
Preservative, colour, fragrance	q.s.
Water, minors	to 100%



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Example 5

A hair conditioning composition was prepared by mixing the following components in the amounts stated.

5

<u>Component</u>	<u>% by weight</u>
Cetyl trimethylammonium chloride (25% a.i.)	4.0
10 Cetearyl alcohol	3.2
Stearyl stearate	0.7
15 Paraffin wax	1.0
Hydroxyethylcellulose	0.35
Cetyl hydroxyethylcellulose	0.03
20 Extrcat of Example 1	0.25
Preservative, colour, fragrance	q.s.
25 Water, minors	to 100%

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CLAIMS

1. A hair treatment composition suitable for application to dark hair, which composition comprises at least one melanin or melanin-type compound, characterised in that the melanin or melanin-type compound is of botanical origin.  
5
2. A hair treatment composition according to claim 1, in which the source of melanin or melanin-type compounds of botanical origin is a blend comprising three types of botanical extract, said types being extracts of  
10 plants belonging to the *Papilionoidea*, *Violacea*, and *Ericaceas* families respectively.
3. A hair treatment composition according to claim 2, in which the blend is a hydroglycolic extract of plants selected from at least three, most preferably all four, of the following species: *Viola*(violet), *Vaccinium myrtillus* (bilberry), *Indigofera tinctoria*(indigo) and *Sarathamnus scoparus*.
4. A hair treatment composition according to claim 3, in which the blend is incorporated at a level of from 0.03 to 5%, preferably 0.005 to 2%, ideally 0.01 to 1%, by weight based on the total weight of the hair treatment composition.
5. A hair treatment composition according to any preceding claim which is in the form of a shampoo composition and which further comprises one or more cleansing

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surfactants, a cationic polymer and emulsified particles of silicone.

6. A hair treatment composition according to any of claims 1 to 4 which is in the form of a conditioner and which further comprises one or more conditioning surfactants, a fatty alcohol and emulsified particles of silicone.
7. Use of a composition according to any preceding claim for the protection of hair against exposure to ultraviolet radiation.
8. Use of a composition according to any preceding claim for imparting a blue shine to hair.